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Triplet extinction coefficients of some laser dyes I

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We measured the triplet extinction coefficients ϵ_T over the laser action spectral region of Rhodamine 6G; Rhodamine B; Rhodamine 110; Fluorol-7GA; Coumarin 540A; Coumarin 522; Coumarin 1; Coumarin 120; 4,4'-diphenyl stilbene; and 2,7-bis-(4-methoxy-phenyl)-9,9-dipropylfluorene. We employed the different lines from an argon ion cw laser for excitation. McClure's method was used to obtain the triplet extinction coefficients ϵ_T . The method requires the measurement of triplet optical densities OD_T as a function of different cw laser excitation intensities (powers) I_{ex} . The importance of triplet-state losses on dye laser efficiency is reviewed. The laser action properties of the laser dyes we studied are briefly discussed as they relate to the measured ϵ_T values.

1. INTRODUCTION

For flashlamp pumped dye lasers, the negative effect of triplet state losses on laser action efficiency is well known.^{1,2} Oscilloscope traces of laser pulses showed that laser action diminishes much sooner than the flashlamp excitation pulse. This effect was attributed to the buildup of triplet-state dye molecules during the excitation from the flashlamp pulse. These triplet-state molecules absorb the laser light more or less efficiently, depending on the number (concentration) N_T of triplet-state dye molecules generated during excitation and the magnitude of their triplet absorption (extinction) coefficient $\epsilon_T(\lambda_{las})$ over the fluorescence (laser action) spectral region. Therefore, triplet-state losses (TSL) are given by the product

$$TSL = N_T \epsilon_T(\lambda_{las}). \quad (1)$$

N_T is determined by the rate equation

$$\frac{dN_T}{dt} = N_S k_{ISC} - \frac{N_T}{\tau_T}, \quad (2)$$

which describes population and depopulation of the lowest energy triplet state T_1 . k_{ISC} is the intersystem crossing rate constant. N_S is the population (concentration) in the first excited singlet state S_1 and depends on the intensity and shape of the excitation pulse. τ_T is the triplet-state lifetime. For long flashlamp pulses ($t > 10^{-6}$ s) or cw laser excitation, we have $dN_T/dt = 0$ and the TSL are given by

$$TSL = N_T \epsilon_T = N_S k_{ISC} \epsilon_T \tau_T. \quad (3)$$

Therefore, to describe quantitatively laser action parameters such as laser action efficiency, laser action threshold, etc., of a laser dye used as an active medium in a dye laser, one must know the values of k_{ISC} , ϵ_T , and τ_T . Unfortunately, there is a critical lack of experimental data on all three of these spectroscopic parameters. This makes a quantitative evaluation of laser dye performance impossible in most cases.

To obtain efficient laser action, one generally is interested in laser dyes that have a high quantum fluorescence yield ϕ_F ($\phi_F \approx 1$). The reason is that k_{ISC} and ϕ_F are related by the approximate relationship³

$$\phi_F = 1/(1 + \tau_F k_{ISC}), \quad (4)$$

or

$$k_{ISC} = (1 - \phi_F)/\tau_F \phi_F, \quad (5)$$

which neglects excited singlet-state S_1 nonradiative transitions to the ground state S_0 . For $\phi_F \approx 1$, Eq. (4) reduces to

$$k_{ISC} = (1 - \phi_F)/\tau_F. \quad (6)$$

τ_F is the fluorescence lifetime, which is generally in the 5×10^{-9} s range. Experimentally, τ_F is not too difficult to measure. Equation (6) explains why a high-quantum-efficiency ϕ_F is equivalent to the presence of a small intersystems crossing rate constant k_{ISC} . From a practical point of view, Eq. (6) is, in many cases, useless. It is experimentally rather difficult to measure quantum fluorescence yields ϕ_F better than $\pm 2\%$.⁴ For example, if the true value of the ϕ_F is 0.98, one would measure all values between 0.96 and 1.00, which would yield meaningless information on k_{ISC} . ϕ_F (and to a certain degree τ_F) is also solvent dependent.

Triplet-state lifetimes τ_T of organic compounds in solutions at room temperature are generally measured by employing flash photolysis equipment.^{5,6} These experiments are rather difficult for triplet-state lifetimes τ_T in the range of 10^{-5} to 10^{-7} s. This is the range of lifetimes one encounters for laser dyes in solutions and when triplet-state quenchers, such as oxygen from air, are present. τ_T also strongly depends on the solvent employed. The knowledge of τ_T values is not necessary for dye laser systems that employ short pulse (laser or flashlamp) in the 100-ns and shorter pulse duration region.⁷

Similarly, experimental values of $\epsilon_T(\lambda_{las})$ for most of the presently used laser dyes are also not available. It is this scarcity that prompted our study. However, there is a second reason.

For efficient laser action to occur, triplet-state losses TSL must be very low. From Eq. (4), this implies that k_{ISC} , τ_T , and ϵ_T must be small. Pavlopoulos proposed^{8,9} that laser action efficiency of laser dyes could be improved by synthesizing new laser dyes, which had lower $\epsilon_T(\lambda_{las})$ values than those presently found in commercially available laser dyes. This conclusion was derived from an examination of the few $\epsilon_T(\lambda_{las})$ values on laser dyes available in the literature.

Therefore, measuring values of $\epsilon_T(\lambda_{\text{las}})$ on a rather large number of known laser dyes would answer the following question: are these values really low? If not, finding or synthesizing new laser dyes with lower $\epsilon_T(\lambda_{\text{las}})$ would make sense. It would lead to dyes that would have superior laser action efficiencies than those presently available from commercial sources.

Schaefer proposed to improve the performance of laser dyes by reducing their triplet-state lifetimes τ_T .¹⁰

For later reference, we define very strong, strong, etc., for conventional singlet as well as triplet absorption, expressed in decadic extinction coefficients [liter (l)/mole cm] as follows:

$\epsilon = 1 \times 10^4 - 1 \times 10^5$	very strong absorption,
$\epsilon = 1 \times 10^3 - 1 \times 10^4$	strong absorption,
$\epsilon = 1 \times 10^2 - 1 \times 10^3$	medium absorption,
$\epsilon = 10 - 1 \times 10^2$	weak absorption,
$\epsilon = \text{below } 10$	very weak absorption.

II. MEASUREMENT OF TRIPLET EXTINCTION COEFFICIENTS OF LASER DYES BY MCCLURE'S METHOD

Several methods are available to measure the triplet extinction coefficients of organic compounds.⁶ McClure's method¹¹ allows the measurement of triplet extinction coefficients, for spectral regions only, which do not overlap with conventional (S-S) absorption. This is not a limiting factor for laser dyes, because one is mainly interested in $\epsilon_T(\lambda)$ values over the fluorescence (laser action) spectral region. Basically, the method requires the generation of a high concentration of triplet-state molecules N_T and steady-state excitation. This is conveniently accomplished by employing a cw laser as excitation source and focusing the laser light with the aid of a lens on the sample.¹² McClure's relationship holds only for small concentrations N_S , no appreciable photodecomposition, and for uniform excitation areas.

McClure derived his simple and very useful relationship by considering all the rate equations that cover the population and depopulation routes of an excited organic molecule in the singlet as well as in the triplet manifold. The following simple linear equation holds:

$$\frac{1}{OD_T} = \left(\frac{1}{\epsilon_T N_S d} \right) \left(1 + \frac{A_T}{I_{\text{ex}}} \right). \quad (7)$$

A_T is a constant that depends on the different rate constants k_i . One only records triplet optical densities OD_T at a fixed wavelength (e.g., at a triplet absorption maximum) as a function of the different cw laser excitation intensities (powers) I_{ex} . A plot of $1/OD_T$ against $1/I_{\text{ex}}$ yields a straight line. Extrapolating to the intersection with the ordinate (i.e., $1/I_{\text{ex}} = 0$, or $I_{\text{ex}} = \infty$) yields $1/OD_T^\infty$. OD_T^∞ is the triplet optical density at infinite excitation intensity I_{ex} . At infinite excitation intensity I_{ex} , the concentration of triplet-state molecules N_T is equal to the original ground-state concentration N_S . One can easily calculate ϵ_T from the relationship $\epsilon_T = OD_T^\infty / N_S d$, with d the thickness of the sample.

Equation (7) does not contain any expression that depends on the actual value I_{ex} (laser power/excitation area)

or A_T . Using different illumination densities, the validity of McClure's method can be tested. These different illumination densities can be obtained easily by setting the lens that focuses the cw laser light at different distances from the sample.¹² Plotting the different $1/OD_T$ values against $1/I_{\text{ex}}$ always yielded straight lines, all of them converging well to one intercept point $1/OD_T^\infty$. In addition, regardless of the concentration N_S used for the experiment, one should always obtain the same value for ϵ_T . The method was tested on anthracene and pyrene. The values of ϵ_T measured agreed well with values obtained by other methods.¹²

Another important parameter is the size of the excitation spot, which can be estimated from an expression derived by Kogelnik and Li.¹³ Focusing a laser beam of Gaussian intensity profile with the aid of a lens will also produce a laser beam with Gaussian intensity profile. The waist w_0 at $1/e^2$ intensity is given by the expression

$$w_0^2 = w^2 [1 + (\pi w^2 / \lambda_{\text{cw}} R)^2]^{-1}, \quad (8)$$

where λ_{cw} is the laser wavelength and R is the wavefront curvature. w is the radius at which the intensity of the laser beam has decreased to $1/e^2$ (the beam diameter). As long as the size of the excitation area on the sample was not below a critical size (the size of the hole in the dovetail plate in front of the monochromator slit), all straight lines converged well into only one value of $1/OD_T^\infty$.¹²

III. EXPERIMENTAL PROCEDURES

A. Concentration ranges

The ranges of dye concentrations available for the experiments was actually rather limited. At the temperature of liquid nitrogen (i.e., 77 K), the solubility of the dyes we studied in the glassy solvents employed was not too high. If one starts out with a concentration N_S (RT) at room temperature, which is higher than the unknown saturation concentration N_S (sat) at 77 K, meaningless results are obtained. We have N_S (RT) > N_S (sat) and the obtained ϵ_T values are smaller than the one that one would have been obtained if all the dye had stayed in solution. This is simply a consequence of equation $\epsilon_T = OD_T^\infty / N_S d$. We therefore always performed measurements on two different concentrations N_S (I) and N_S (II). If the higher concentration was II and saturation occurred at 77 K, one would find ϵ_T (II) < ϵ_T (I). In this case, we would disregard ϵ_T (II). If both concentrations N_S (I) and N_S (II) were higher than N_S (sat), one should observe the same intercept point $1/OD_T^\infty$ (I) = $1/OD_T^\infty$ (II). This is because N_S (sat) should be the same in both experiments. In this case, one has to perform another experiment at even lower concentration.

With the glassy solvents we employed, the highest concentration was generally 2×10^{-4} mol. The lowest concentration we attempted was in the range of 5×10^{-5} mol. However, at this concentration, considerable laser excitation light would pass through the sample unabsorbed.

Cooling the sample down to 77 K causes the dye solution to contract. Therefore, one measures $\bar{\epsilon}_T$ values that are higher than would be observed performing the experiments at room temperature. The contraction coefficients ρ for the

glassy solvents employed was determined and used to calculate ϵ_T values based on N_S (RT):

$$N_S(77\text{ K}) = \rho N_S(\text{RT}), \quad \text{or} \quad \epsilon_T = \rho \bar{\epsilon}_T. \quad (9)$$

B. Recording triplet optical densities OD_T

Triplet optical densities $\text{OD}_T(\lambda)$ are similarly defined as conventional (singlet) densities, namely

$$\text{OD}_T(\lambda) \equiv \log I_0/I = N_T \epsilon_T(\lambda) d. \quad (10)$$

I_0 is the intensity of the monitoring light source after passing through the sample and I is its intensity with the cw laser excitation on. It should be noted that expression (10) is the same as expression (1).

For excitation, the wavelength λ_{ex} we used was the one available from the cw argon ion laser that came closest to the absorption maximum of the strong, lowest-energy S - S absorption band of the dye. To measure values of $\epsilon_T(\lambda_{\text{las}})$, we used the following procedure. We recorded $\epsilon_T(\lambda_{\text{las}})$ at fixed wavelengths at intervals of 20 nm. The wavelength range we covered was taken from the tuning curve shown in the EXCITON Laser Dye catalog under Lasing Wavelength Range (nm). For example, for Fluorol 555 (Fluorol-7GA), the shortest lasing wavelength is 518 nm for a XeCl(308) pump source and the highest is 608 nm for a flashlamp (Fl) pump source. Consequently, we measured OD_T from 520–620 nm in 20-nm intervals and present the $\epsilon_T(\lambda_{\text{las}})$ values for these wavelength intervals in Table I. In between wavelengths can be obtained by interpolation. All the OD_T values were measured at a wavelength λ_i that was at the long-wave-

length side of the tuning region λ_{las} . Where possible, we measured OD_T at a T - T absorption maximum. For the xanthene laser dyes, however, OD_T values were obtained, where T - T absorption was lower than the one present over the laser action spectral region.

To obtain the intercept point $1/\text{OD}_T^x$ we always recorded five $1/\text{OD}_T^x$ values by varying I_{ex} , the cw laser excitation intensity (power), by a factor of 5. For example, if the highest cw laser power used was $I_{\text{ex}} = 50$ mW, we would perform measurements at 25, 16.7, 12.5, and 10 mW in order for the $1/I_{\text{ex}}$ points to be equidistant from each other. However, we used only the first four points, disregarding the one obtained with the lowest power. Since a straight line is completely determined by two points, one needs only two $1/\text{OD}_T$ values to extrapolate to the ordinate to obtain $1/\text{OD}_T^x$. Because of photodecomposition, noise from the liquid nitrogen, intensity fluctuations of the monitoring light source, etc., one would like to use more than two points to average over measurement errors. But with decreasing intensity I_{ex} , the signal-to-noise ratio in the obtained $1/\text{OD}_T$ values gets larger and larger, exerting a disproportionately large effect on the location of the intercept point $1/\text{OD}_T^x$. We obtained much better agreement among different $1/\text{OD}_T^x$ values we measured by dropping the fifth (largest) $1/\text{OD}_T$ value.

We used a pocket calculator and the method of linear regression to find the intercept points $1/\text{OD}_T^x$.

C. Photodecomposition

The main reason why we could not measure triplet extinction coefficients of many coumarin laser dyes, POPOP,

TABLE I. Measured triplet extinction coefficients ϵ_T of laser dyes as function of wavelength λ_{las} . λ_i (nm) is the wavelength at which $1/\text{OD}_T$ was measured. I_{ex} is the maximum cw laser power (in mW) employed for excitation. λ_{ex} (nm) is the wavelength of the exciting cw laser line.

Laser dye	λ_{las} (nm)						λ_i (nm)	I_{ex} (mW)	λ_{ex} (nm)
	$\epsilon_f (1 \cdot 10^{-3} \text{ l/mole cm})$								
Rhodamine B	580	600	620	640	660	680	50		528.7
	12.5	12.5	12.1	11.6	10.2	6.9			
Rhodamine 6G	550	570	590	610	630	650	50		528.7
	8.7	9.0	9.7	9.4	9.7	8.3			
Rhodamine 110	530	550	570	590	610	590	100		501.7
	6.8	7.6	7.9	7.5	7.4	7.5			
Fluorol-7GA	520	540	560	580	600	640	50		457.9
	3.7	3.1	3.2	3.1	2.6	3.8			
Coumarin 540A	500	520	540	560	600	580	100		351.1/ 363.8
	1.9	2.1	2.3	2.6	2.7	2.9			
Coumarin 522	480	500	520	540	560	580	50		351.1/ 363.8
	1.4	1.8	2.7	2.6	2.5	3.2			
Coumarin 1	460	480	500	520	540	585	50		351.1/ 363.8
	0.9	1.3	1.9	2.4	3.4	5.3			
Coumarin 120	420	440	460	480	500	575	20		351.1/ 363.8
	0.9	0.9	1.0	1.6	2.7	7.1			
Diphenyl Stilbene	400	420	440	460	480	500	100		351.1/ 363.8
	6.1	11.0	25.6	42.9	46.2	94.4			
2,7-bis (4-methoxy- phenyl)-9,9- dipropylfluorene	380	400	420	440	460	580	0.5		351.1/ 363.8
	1.3	1.3	1.9	2.0	2.5	19.2			

and some other laser dyes, was photodecomposition. It should be emphasized that photodecomposition, as it applies to laser dyes, is actually the combination of two effects. One is true photodecomposition of a molecule because of absorbed radiation. The result is reduced concentration of the original compound. The second effect is the formation of decomposition products, which absorb the laser radiation. If this absorption is strong, minute amounts of the decomposition product will affect laser action efficiency as well as our experimental results, even though the original concentration of the dye itself has only been reduced by a small amount.

These two effects were amplified in our experiments with laser dyes, which had a long triplet-state lifetime (phosphorescence) τ_p (in the range of 1 s), but only moderate decomposition rates. Upon excitation of the sample with cw laser light, steady-state condition is reached only after several seconds. This was often sufficient time for the accumulation of excessive amounts of photodecomposition products, or reduction in dye concentration, or both, yielding unacceptable data.

To reduce photodecomposition effects on the measurement accuracy of OD_T , we used the following procedures. We performed experiments at fixed wavelengths only. We also tried to conduct measurements as quickly as possible. If, after recording I_0 and I , I_0 was not quite reproduced because of the formation of some photodecomposition products, we would raise the liquid nitrogen dewar flask, together with the sample, about $\frac{1}{2}$ mm. This would make available an excitation area without photodecomposition products from the previous experiment. If the discrepancy between I_0 and the I_0 recorded after cutting off the cw laser excitation light was too large, we would discard the laser dye.

For most of the laser dyes we studied, there was some difference between the original I_0 and the I_0 recorded after shutting off the excitation. This, of course, was also dependent on the spectral region studied. Because of the difficulty in estimating experimental errors arising from some photodecomposition, no measurement error analysis on our ϵ_l values was performed.

D. Spectroscopic equipment

We used the same setup as employed in Ref. 12, except that we replaced the Spectra Physics model 164 cw krypton ion laser with a model 2025-05 cw argon ion laser.

A 350-mm-focal-length planoconvex quartz lens was used to focus the cw laser light on the sample surface. The lens was positioned 250 mm from the sample surface to produce a somewhat enlarged excitation area on the sample. As pointed out earlier, it is important that the diameter of the excitation area projected on the hole of the dovetail plate be larger than the diameter of the hole.

E. Chemicals

Rhodamine 6G, Rhodamine B, Rhodamine 110, Coumarin 1, and Coumarin 120 were obtained from Eastman Kodak Company, and Coumarin 522 and Coumarin 540A

from Exciton. 4,4'-diphenyl stilbene was purchased from J. T. Baker Chemical Company and recrystallized from benzene. Fluorol-7GA was furnished by the GAF Corporation and was recrystallized five times from ethanol.

2,7-bis(4-methoxyphenyl)-9,9-dipropylfluorene was supplied by Kauffman. With the exception of diphenyl stilbene and 2,7-bis(4-methoxyphenyl)-9,9-dipropylfluorene, all compounds were dissolved in ethyl alcohol (from U.S. Industrial Chemicals Company) and methyl alcohol (from Aldrich Chemical Company) in the ratio 4:1. The contraction coefficient ρ for this mixture was 0.79. Diphenyl stilbene was dissolved in a mixture of 2-methyltetrahydrofuran (from Lancaster Chemical Company) and toluene (from Matheson, Coleman & Bell) in ratio 1:1. The ρ for this mixture was 0.80. 2,7-bis(4-methoxyphenyl)-9,9-dipropylfluorene was dissolved in 2-methyltetrahydrofuran as glassy solvent, which had $\rho = 0.84$.¹²

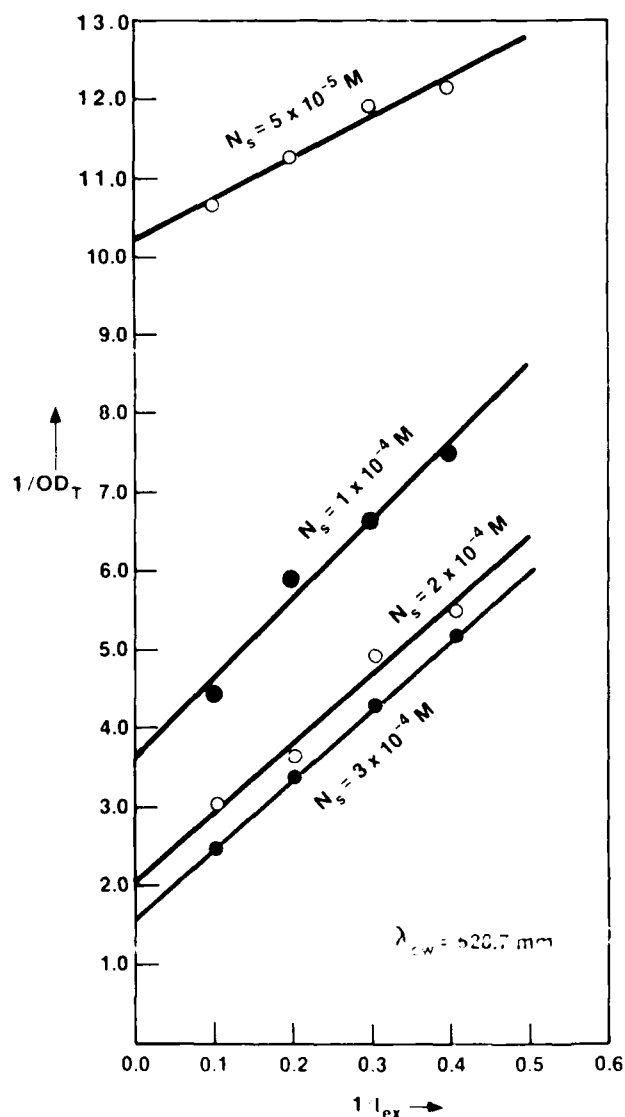


FIG. 1. Plot $1/OD_T$ vs $1/I_{ex}$ to obtain $1/OD_T$ by extrapolation for Rhodamine 6G. N_s presents the room temperature concentrations. λ_{cw} presents the cw laser excitation wavelength.

IV. RESULTS AND DISCUSSION

A. Triplet extinction coefficients

1. Rhodamine 6G

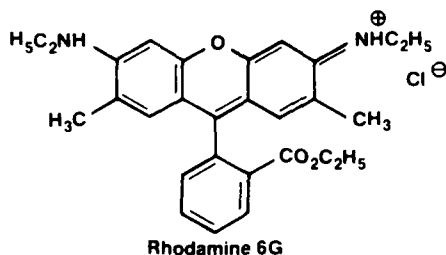
Among laser dyes, Rhodamine 6G holds a special position. It is one of the most efficient laser dyes presently known and also has good photochemical stability. It has been known to exhibit laser action since 1967.¹ Any new laser dye claiming superior performance must measure up to Rhodamine 6G.

With our equipment, T - T absorption of Rhodamine 6G (as well as of the other xanthene laser dyes we studied) was easy to observe because of the relatively long triplet (phosphorescence) lifetime τ_p (in the second range). This, together with good photostability in the glassy solvent, was the main reason for the good reproducibility of the spectroscopic data we recorded. An $\epsilon_T(590 \text{ nm}) = 1.3 \times 10^4 \text{ l/mole cm}$ (see Buettner *et al.*¹⁴).

Figure 1 presents a typical $1/\text{OD}_T$ plot against $1/I_{\text{ex}}$, using different Rhodamine 6G concentrations N_s (RT). For excitation, the $\lambda_{\text{ex}} = 528.7\text{-nm}$ line was employed and $\lambda_i = 650 \text{ nm}$. Using the resulting intercept points $1/\text{OD}_T^z$, one obtains the following $\epsilon_T(650)$ values: 7.6, 8.3, 7.3, and $7.6 \times 10^3 \text{ l/mole cm}$ for the 5×10^{-5} , 1×10^{-4} , 2×10^{-4} , and 3×10^{-4} molar solutions. Because the 1×10^{-4} molar solution yields the highest ϵ_T value, we list it in Table I, discarding all the others obtained with higher concentrations.

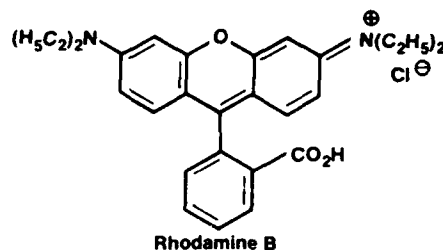
We also did not use the value obtained from the 5×10^{-5} molar solution. At this low concentration, the laser light was only partially absorbed, yielding small OD_T values. Measurement errors (e.g., noise) are probably responsible for the discrepancy. We did not perform experiments at this low concentration for any of the other dyes we studied.

Our value of $\epsilon_T(590 \text{ nm}) = 9.7 \times 10^3 \text{ l/mole cm}$ agrees fairly well with the one obtained by Ref. 14.



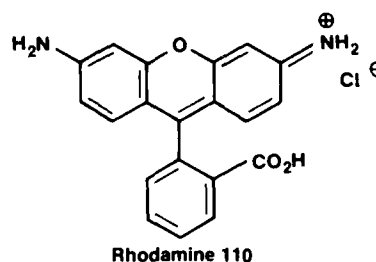
2. Rhodamine B

Laser action from this laser dye was first observed by Schmidt and Schaefer.² This laser dye was of good photochemical stability. Our value for $\epsilon_T(610 \text{ nm}) = 12 \times 10^3 \text{ l/mole cm}$ agrees well with $14 \times 10^3 \text{ l/mole cm}$ measured by Ref. 14. The higher quantum fluorescence yield $\phi_f = 0.84$ (Ref. 14) and the lower $\epsilon_T(\lambda_{\text{exc}})$ of Rhodamine 6G could explain its somewhat better laser action properties compared to Rhodamine B, which has a $\phi_f = 0.62$.¹⁴



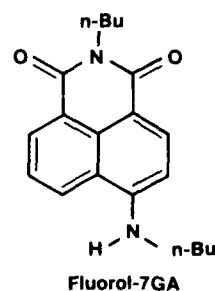
3. Rhodamine 110

Rhodamine 110 (Ref. 15) was another stable laser dye we studied. Performing three independent measurements with 1×10^{-4} mol solution, we obtained for $\epsilon_T(590)$: 8.9, 8.9, and $9.0 \times 10^3 \text{ l/mole cm}$. Using a 2×10^{-4} mol solution, we found $\epsilon_T(590) = 9.7 \times 10^3 \text{ l/mole cm}$. The value for $\epsilon_T(590)$ shown in Table I is the average of all four measurements.



4. Fluorol-7GA

Laser action under flashlamp excitation from this compound was reported by Lambropoulos.¹⁶ This dye was rather stable photochemically. The $\epsilon_T(640)$ value shown in Table I is the average from the two measurements at 1 and 2×10^{-4} mol solution, which yielded $\epsilon_T(640) = 4.5$ and $5.0 \times 10^3 \text{ l/mole cm}$.

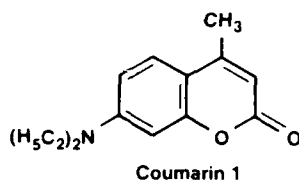


5. Coumarin 1

Coumarin 1 (7-diethylamino-4-methyl coumarin) was the first coumarin derivative from which Sorokin and Lankard¹⁷ observed laser action. Since then, about 100 coumarin laser dyes have come to be known.¹⁸ Their laser action wavelengths cover the spectral region from about 440 to 540 nm. Among the several coumarin laser dyes we tested, Coumarin 1 belonged to the few that were fairly stable photochemically. We spent considerable effort measuring the $\epsilon_T(\lambda_{\text{exc}})$ values of this compound, because the values we obtained deviated

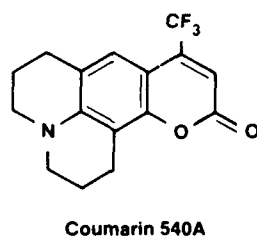
ed considerably from the ones obtained by Dempster *et al.*¹⁹ [$\epsilon_f(620) = 22 \times 10^3$ l/mole cm] and Pavlopoulos²⁰ [$\epsilon_f(585) = 19 \times 10^3$ l/mole cm] for the *T-T* absorption maximum. Our values were considerably lower; specifically, those with the 1×10^{-4} and 2×10^{-4} molar solution. We measured $\epsilon_f(585) = 6.6$ and 6.6×10^3 l/mole cm, respectively. The $\epsilon_f(\lambda_{las})$ for the four coumarin dyes we measured are all in about the same range, and we do not believe that photodecomposition is responsible for the difference with the values reported in Refs. 19 and 20.

Perhaps the deviation could have resulted from the employment of the depletion method, as discussed in Refs. 12 and 21. It is well known that, when there is some overlapping of *S-S* with some *T-T* absorption, questionable ϵ_f values may be obtained.



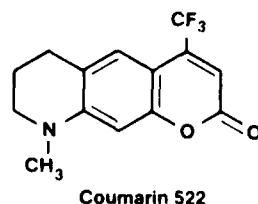
6. Coumarin 540A

Coumarin 540A (Ref. 22) was photochemically rather stable with the exception of the 480-nm spectral region. The 2×10^{-4} molar solution yielded $\epsilon_f(580) = 3.3 \times 10^3$ l/mole cm, but the 1×10^{-4} molar solution yielded $\epsilon_f(580) = 3.9 \times 10^3$ l/mole cm. Because the lowest concentration gave a higher value, the $\epsilon_f(\lambda_{las})$ values shown in Table I are derived from the latter concentration only.



7. Coumarin 522

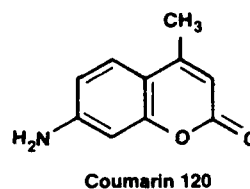
Coumarin 522 (Ref. 22) is another coumarin dye that is photochemically fairly stable. Two different 2×10^{-4} molar solutions gave $\epsilon_f = 3.5$ and 3.8×10^3 l/mole cm. We discarded both values, since the one obtained from a 1×10^{-4} molar solution $\epsilon_f(580) = 4.4 \times 10^3$ l/mole cm was lower; it is therefore used in Table I.



8. Coumarin 120

Coumarin 120 (Ref. 15) was photochemically somewhat unstable. The two concentrations 1 and 2×10^{-4} molar

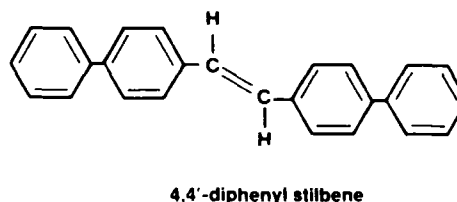
solutions resulted in the two $\epsilon_f(575)$ values of 8.2 and 9.8×10^3 l/mole cm. The average of both values is shown in Table I.



9. Diphenylstilbene

Laser action from this compound was first observed by Furumoto and Ceccon,²³ employing a short-duration (50 ns) flashlamp. The sulfonated derivative of this molecule (known as Stilbene 1), which exhibits improved solubility, is a widely used laser dye showing efficient laser action under ultraviolet cw laser excitation.²⁴ Stilbene 1 could not be dissolved in sufficient concentration in glassy solvents. However, diphenylstilbene could be dissolved in a mixture of 2-methyltetrahydrofuran: toluene (ratio 1:1), and showed good photostability under ultraviolet cw laser excitation.

Both compounds show strong fluorescence. Furthermore, their triplet-state lifetimes τ_T should be very small, since both are stilbene derivatives.²⁵ The fluorescence (laser action) spectral region also falls on declining *T-T* absorption. It falls on the tail of a *T-T* absorption band with its intensity maximum at about 500 nm.²⁵ It is difficult to understand why this laser dye does not show efficient laser action in conventional dye laser systems, which employ flashlamps with 200- to 500-ns risetimes. However, according to our measurements shown in Table I, *T-T* absorption (expressed in ϵ_f) is not small for this compound. The *T-T* absorption maximum at 500 nm has an ϵ_f of about 1×10^5 l/mole cm, which represents a very strong absorption. And although *T-T* absorption over the 400- to 460-nm spectral region has considerably declined, the $\epsilon_f(\lambda_{las})$ values over this region are still rather high (see Table I). This may explain the rather high laser action threshold of this laser dye.



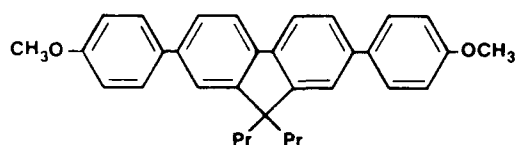
10. 2,7-bis(4-methoxyphenyl)-9,9-dipropylfluorene

This new dye²⁶ presents a realization of improved laser dyes, suggested by Pavlopoulos and Hammond,⁸ and exhibiting a favorable A_2c constellation. To improve the laser action properties of *p*-quaterphenyl (and similar chromophores), substitution in the *p,p'*-position by auxochromic groups (e.g., $-OCH_3$) is made, in addition to rigidization of the phenyl groups of the molecule by bridging them with $>CH_2$ group(s). Auxochromic group substitution moves the strong lowest energy absorption band to longer wave-

lengths (bathochromic effect). The shifting of the absorption band to longer wavelengths also shifts the fluorescence spectrum to longer wavelengths. The $>\text{CH}_2$ group(s) bridging the phenyl groups keep the molecule planar, which results in maintaining a high quantum fluorescence yield ϕ_F . In addition, solubility of the laser dye is also improved.²⁶ Laser action properties of other substituted quaterphenyls and related molecules have been reported by Guesten and co-workers.^{27,28}

In addition, *p*-quaterphenyl presents a chromophore, where the fluorescence intensity maximum is positioned at a considerable distance (i.e., large energy separation ΔE) from the *T-T* absorption intensity maximum. It therefore presents a typical chromophore, where long-axis (i.e., in the *p,p'*-position) auxochromic group substitution should yield an efficient laser dye.^{20,29} A red shift of all electronic transitions results, maintaining the large energy separation ΔE . Consequently, and as seen in Table I, low *T-T* absorption [i.e., small $\epsilon_T(\lambda_{\text{las}})$] is present over the laser action spectral region, which results in the exceptional laser action properties of this new laser dye. Again, this conclusion rests on the assumption that the quantum fluorescence yield ϕ_F is high (or, more accurately, k_{ISC} remains small).

This compound was relatively stable under cw ultraviolet laser light illumination. The reported $\epsilon_T(\lambda_{\text{las}})$ value is the average from measurements on 1 and 2×10^{-4} molar solutions.



2,7-bis(4-methoxyphenyl)-9,9-dipropyfluorene

B. Discussion

From the $\epsilon_T(\lambda_{\text{las}})$ values on laser dyes we collected in Table I, it is apparent that they are not really small. The lowest value is $0.9 \times 10^3 \text{ l/mole cm}$ for some of the coumarin laser dyes and goes up to about $12 \times 10^3 \text{ l/mole cm}$ for Rhodamine B. From our definition of very strong, strong, etc., absorption, most of these $\epsilon_T(\lambda_{\text{las}})$ values fall under the definition of strong absorption. If laser dyes were available with ϵ_T values falling into the lower part of the "medium absorption" range, much more efficient laser action should be observable. There is no obvious theoretical criterion that states that *T-T* absorption over the laser action spectral re-

gion cannot have small ϵ_T values. Employing these improved laser dyes, efficient cw laser action with noncoherent sources,³⁰ or with sunlight as the pump source, might be possible.

ACKNOWLEDGMENT

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